

## IV.F.5 Quick-Starting Fuel Processors - A Feasibility Study

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### Objectives

- Study the feasibility of fast-starting fuel processors such that they can meet DOE's goals for on-board fuel processors.
  - 60 seconds to generate 90% of rated hydrogen flow (for the year 2005).
- Assess the energy consumption of on-board fuel processors during a cold start from ambient temperatures of 20°C.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- I. Fuel Processor Start-up/Transient Operation
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration and Efficiency

### Approach

Design a fuel processor capable of fast-start, and experimentally study the performance of a sub-scale unit in the laboratory.

- Design a fast-starting fuel processor using state-of-the-art component technologies.
  - 140 SLPM of hydrogen in 60 seconds from gasoline fuel.
- Build and test the components and the integrated fuel processor with collaboration and support from national laboratories, private industry, and universities.
- Develop and validate models for the design, operation, and control of integrated, fast-start fuel processors.
- Estimate start-up fuel consumption based on laboratory hardware, and evaluate means to decrease start-up fuel consumption through analyses of fuel processor design and hardware alternatives.

### Accomplishments

- Experimentally demonstrated the autothermal reformer (ATR) zone reformat contained 30% hydrogen at 51-65% of the rated hydrogen capacity within 60 seconds after fuel injection. Faster (10-20 s) response projected with reconfigured ATR and feed delivery.
- Demonstrated ignition of reformat from ATR, containing ~10% CO, at shift reactor zone.
- Estimated start-up fuel energy needs for the components and the integrated fuel processor hardware for the laboratory unit and projected for an automotive design.

- Identified and analyzed a potential configuration that offers a start-up fuel energy consumption of approximately 1.7 MJ per cold start, for a 50 kW<sub>e</sub> fuel processor.

### **Future Directions**

- Reconfigure fuel processor design to reduce start-up time and lifetime fuel consumption for the automotive application.
- Reduce thermal mass of fuel processor components.
- Develop nozzles that can deliver well-mixed reactant streams that contain both liquids and gases, uniformly across the catalyst face.
- Apply validated models to control the start-up transition.

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### **Introduction**

Fast-starting capability is an identified technical barrier for on-board fuel processing. DOE has set a cold-start (from ambient temperature of 20°C) target of 60 seconds for the year 2005. The principal constraint in meeting this target is the large thermal mass of the fuel processor, with some zones that operate at temperatures of 700°C or more. Reaching the operating temperature within the targeted start-up time requires rapid heating and associated fuel energy.

The objective of this work is to study the feasibility of developing fast-starting fuel processors that can meet DOE's targets, to investigate designs and strategies capable of meeting the start-up targets, and to validate models using experimental and hardware data.

### **Approach**

The approach used was to design a fuel processor that would allow for parallel heating of the specific fuel processor zones that are essential to meeting the quantity (90% of the rated hydrogen capacity) and quality (containing more than 30% hydrogen and less than 50 ppm carbon monoxide) of the reformat within the designated start-up time.<sup>1</sup> The experiments were conducted with a laboratory-scale fuel processor designed to convert gasoline to produce 140 SLPM of hydrogen.

A fuel processor system model was set up to size the fuel processor components at the design point and to simulate their performance during the start-up transition. Preliminary data for the components were obtained from the project partners and component suppliers (Los Alamos National Laboratory, Oak

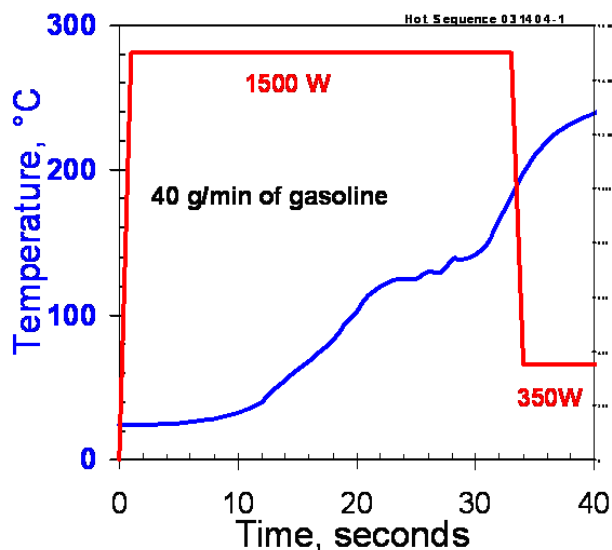
Ridge National Laboratory, Pacific Northwest National Laboratory, ArvinMeritor, Precision Combustion Inc., and Quantum Group). The start-up protocols were then studied through a series of modeling and experimental iterations. Three types of models were used to support this study – a GCtool (system) model, a FEMLAB (integrated components) model, and computational fluid mechanics (three-dimensional flow and heat transfer characteristics) models – and are being validated with the generated experimental data.

### **Results**

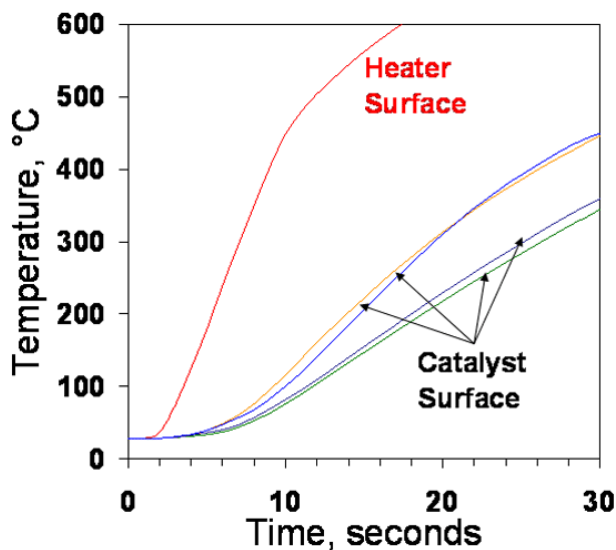
#### *Start-up Experiments*

The start-up strategy consists of readying the ATR as fast as feasible to produce a gas stream containing hydrogen and carbon oxides, and then inject air into the essential catalyst zones downstream such that the oxidation reactions generate localized heat to warm up those specific catalyst locations. Restricting the initial heating to these essential zones limits the fuel and air flow rates during start-up to within the capacity of the fluid handling devices and channels. After the initial start-up period, the other components, all of which contribute to the high efficiency rating of the fuel processor, gradually warm up to their design temperatures.

The rapid readiness of the ATR is contingent on a controlled ignition process, which requires the fuel and air to be mixed and injected onto a heated ATR catalyst surface. Our apparatus was able to pump the air and liquid fuel within 1-2 seconds. An electrically heated vaporizer generated a mixed-phase gasoline stream at 150°C to the ATR in 20 seconds [Figure 1]. The slowest step was heating the front edge of the



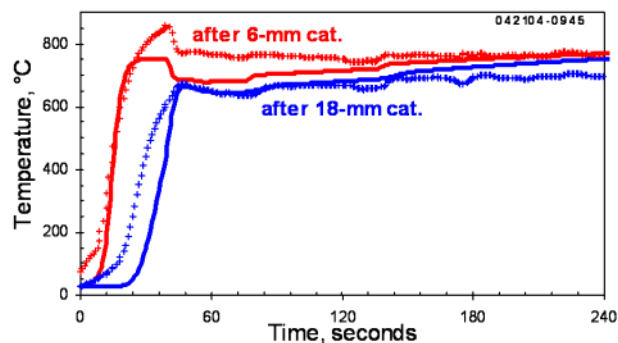
**Figure 1.** Power to the Vaporizer and Resulting Temperature Rise of the Gasoline Stream that Emerges from It



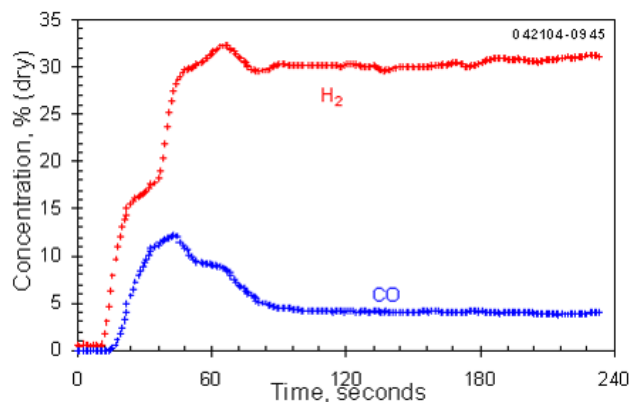
**Figure 2.** Temperature Rise during Catalyst Pre-Heating with 1.2 kW of Electrical Power and 5 L/min of Air

catalyst to 300°C, which was achieved by passing the air over electrical heater coils placed slightly upstream of the catalyst [Figure 2].

A typical start-up process consisted of starting the injection of fuel (40 g/min) and air (O/C=0.5), followed by water injection (S/C=1.2), then adjustment of the feed proportions to control the ATR temperature rise. Figure 3 shows the



**Figure 3.** Temperature Rise in the ATR Catalyst during a Start-Up (points are experimental, lines are modeling results)



**Figure 4.** Concentrations of Hydrogen and Carbon Monoxide in Reformate from ATR at Start-Up

temperature history of the ATR catalyst as a function of time after fuel injection. The thermocouple located at 6 mm from the front face increases to ~700°C in 30 seconds and is limited to below 900°C by the introduction of liquid water. The thermocouple at 18 mm shows a temperature history with a similar, though delayed and damped, trend. Figure 4 shows the concentrations of hydrogen and carbon monoxide in the product gas from the ATR. The introduction of water shows the anticipated rise in H<sub>2</sub> concentration and drop in CO concentration that result from the increased contributions of steam reforming and water gas shift reactions that are favored. The hydrogen concentration is observed to peak at 60 seconds, at which time the hydrogen flow rate is estimated to represent 51-65% of the rated hydrogen capacity of 140 SLPM.

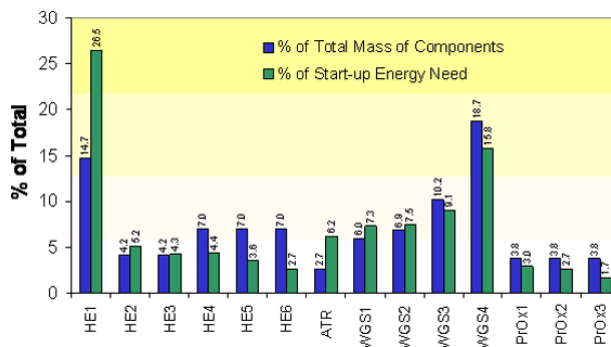
**Table 1.** Masses of the 10-kW<sub>e</sub> Laboratory Fuel Processor Components and the Minimum Thermal Energy Needed to Heat Them to their Design Temperatures

		ATR	WG51	WG52	WG53	WG54	P/Ox1	P/Ox2	P/Ox3
Catalysts									
Component Weight, g		578	1276	1460	2163	3978	800	800	800
Th. Energy Need, kJ		178	210	215	261	454	87	78	48
Heat Exchangers		HE-1	HE-2	HE-3	HE-4	HE-5	HE-6		
Component Weight, g		3140	898	898	1500	1500	1500		
Th. Energy Need, kJ		760	150	124	125	102	78		
		Total = 2870 kJ							

A key part of a successful rapid start is the ability to heat the catalytic zones necessary for CO management. Preliminary tests with air injection at the water gas shift (WGS) assemblies have shown that oxidation reactions can be initiated as soon as the reformat gas stream (from the ATR) arrives. The ability to catalytically initiate the oxidation of a reformat stream containing more than 10% carbon monoxide confirms the ability to locally heat the WGS zones through oxidation reactions, thereby validating the feasibility of our approach. The preferential oxidation (PROx) catalysts have also demonstrated activity with 10% CO at 25°C.

#### Start-up Fuel Consumption

The energy required to heat the fuel processor from ambient temperature to its design temperature is directly proportional to the thermal mass of the fuel processor. Table 1 lists the main components of the fuel processor, their masses (as received), and the minimum amount of energy needed to heat them to their respective operating temperatures. This needed energy adds up to 2.87 MJ for the 10-kW<sub>e</sub> fuel processor hardware we have built. The mass and the fuel energy requirement of this laboratory unit are considerably higher than would be acceptable for a commercial unit, primarily due to the experimental constraints which led to multiple boundaries, heavy walls, and allowances for instrumentation and operational flexibility. Figure 5 shows the component contributions to the mass and the start-up fuel energy consumption. The lowest-temperature shift zone (WGS4) contributes the largest percentage to the mass, while the microchannel heat exchanger (HE1) that follows the ATR requires the most fuel energy as a result of its high operating temperature.



**Figure 5.** Component Contributions to the Mass and Start-Up Energy Needs of a 10-kW<sub>e</sub> (25-kWt) Fuel Processor

An analysis of the fuel cell system with the objective of reducing the lifetime fuel consumption (calculated as a combination of start-up and drive-cycle fuel consumptions) indicates that elimination of WGS4 reduces the drive-cycle efficiency, but improves the lifecycle fuel economy. System models investigating alternative fuel processor configurations that can reduce lifetime fuel consumption have helped to identify designs that can limit the start-up fuel consumption to less than 2 MJ per cold start for a 50-kW<sub>e</sub> fuel processor.

#### Conclusions

- A start-up scheme has been demonstrated for the front section of the fuel processor, with a hydrogen yield of over 50% of the rated hydrogen capacity within 60 s. The hydrogen yield increases when the downstream shift reactors reach active temperatures.
- The readiness of the ATR is limited by the time taken to preheat the catalyst to ignition temperatures.
- The post-ATR heat exchanger and the low-temperature water gas shift reactors represent the highest thermal mass in the fuel processor and, therefore, contribute the most to the start-up fuel energy consumption.
- Optimization of the fuel processor design for lifetime fuel consumption results in configurations that offer lower start-up energy, but which require some tradeoffs with the steady-state fuel processor efficiency.

**References**

1. S. Ahmed, R. Ahluwalia, S.H.D. Lee, "Quick Starting Fuel Processors," FY 2003 Annual Progress Report, Hydrogen, Fuel Cells and Infrastructure Technologies Program, 2003.

**FY 2004 Publications/Presentations**

1. S. Ahmed, R. Ahluwalia, S.H.D. Lee, "Experimental Study to Determine Fast-Start Capability of On-Board Fuel Processors," 2003 Fuel Cell Seminar Abstracts, Miami Beach, FL, 2003.
2. S. Ahmed, R. Ahluwalia, S.H.D. Lee, "Fast-Start Capability of On-Board Gasoline Fuel Processors for Fuel Cell Vehicles," IEA Annex XI-II and XV Meeting, November 8, 2003, Miami Beach, FL.

**Special Recognitions & Awards/Patents Issued**

1. S. Lottes and S.H.D. Lee, Argonne National Laboratory Invention Disclosure, "Method and Apparatus for Uniform Injection into and Vaporization of Water in the Hot Flow of an Annular or High Aspect Ratio Duct."
2. S. Lottes and S.H.D. Lee, Argonne National Laboratory Invention Disclosure, "Method and Apparatus for Uniform Multi-Port Injection into and Mixing of a Second Fluid with the Primary Flow in a Chamber with Small Length to Hydraulic Diameter."